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$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ cathodes incorporated with $Sm_{0.2}Ce_{0.8}O_2$ by three different methods for solid oxide fuel cells

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HIGHLIGHTS

- The incorporation of SDC into LSCF by three methods is comparative studied.
- Reaction happens with YSZ for the mixture LSCF and SDC as cathode.
- LSCF cathode dip coated by SDC has the best electrochemical performance.
- New phase of $SrCrO_4$ is formed on all the cathode surface after 100 h of test.

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ABSTRACT

The incorporation of $Sm_{0.2}Ce_{0.8}O_2$ (SDC) into $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF) is carried out by three methods: mechanical mixing, infiltration, and dip coating. The effects of SDC on the electrochemical performance of the LSCF cathodes are studied by electrochemical impedance spectroscopy (EIS) at 800 °C for 100 h. LSCF mechanically mixed with SDC as the cathode decreases the electrochemical performance of the half-cell; the LSCF cathode infiltrated with SDC offers faster activation and decreased resistance with thermal treatment time; and the LSCF cathode dip coated with SDC has the smallest polarization resistance. These cathodes also show clear microstructure differences at the cathode/interconnect interface after 100 h of thermal treatment. $SrCrO_4$ phase forms on all the cathodes near the interconnect. Reactions between the mechanically mixed cathode and the YSZ electrolyte destroy the electrolyte. The influence of SDC catalyst on oxygen adsorption, dissociation, and incorporation is explained for each type of cathodes. Overall, dip coating method is recommended for incorporation of SDC into the LSCF cathode.

1. Introduction

There are many challenges for the commercial use of solid oxide fuel cells (SOFCs). These include the high operating temperatures to improve the activities of the electrodes and the ionic conductivity of the electrolyte, as well as the degradation of cell materials because of the high temperature and long operating time. To make SOFCs commercially competitive, it is necessary to develop electrode materials with high activity and stability between 500 and 800 °C [1–3].

LSCF is a conductive ABO_3 perovskite ceramic, exhibiting electronic conductivity of 302 $S\ cm^{-1}$ and ionic conductivity of $8 \times 10^{-3}\ S\ cm^{-1}$ at 800 °C [4,5]. Additionally, the thermal expansion coefficient of LSCF is $15 \times 10^{-6}\ K^{-1}$ [6], compatible with that of classic 8 mol% yttria-stabilized zirconia (YSZ, $10.5 \times 10^{-6}\ K^{-1}$) [7]. Because of its mixed ionic and electronic conductivity and compatibility with YSZ, LSCF is widely used for intermediate temperature SOFCs. Unfortunately, the development of LSCF cathodes has been hindered by their performance degradation. Several possible degradation mechanisms have been proposed, such as the instability of LSCF material [8,9], the coarsening of LSCF particle [10,11], the reaction between the LSCF cathode and YSZ electrolyte [12,13], and the chromium poisoning from the interconnect [14,15]. In addition, the oxygen reduction reaction is mainly confined to the electrode/electrolyte interface due to the relatively low ionic conductivity of LSCF, which results in low electrocatalytic activity. Considerable efforts have been devoted to improve the stability and electrocatalytic activity of LSCF cathode. For example, a SDC interlayer on the YSZ electrolyte has been reported to enhance the stability of LSCF [16]. Introduction of oxygen ion conducting phases is another option [17,18].

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Rare earth doped ceria has been considered as one of the most promising electrolyte materials for intermediate temperature SOFCs because of its high ionic conductivity and low electronic conductivity [19]. Also, doping rare earth oxide into ceria can slightly improve its mechanical properties [20]. Among the various dopants, Gd^{3+} and Sm^{3+} doped ceria have been studied extensively owing to their higher conductivity and stability in reducing environments [21,22]. This results from the small association enthalpy between the trivalent dopant cation and the oxygen vacancy as well as the optimum radii of the dopants [23,24]. SDC is also incorporated into cathode materials to improve the stability of the cathodes. The ionic conductivity of SDC is as high as 1.7×10^{-2} S cm^{-1} at ~800 °C [25], much higher than that of LSCF. When introduced into the cathode, SDC can offset the low ionic conductivity of the cathode materials, promote the ionic exchange processes, and expand the electrochemically active area, such as triple phase boundaries (3PBs). These permit electrochemical reactions to occur within the electrodes, thus reducing the polarization resistance [26,27].

There are many methods to incorporate SDC into the LSCF cathode, such as mechanical mixing and infiltration. The electrochemical performance of LSCF mixed with SDC showed small polarization resistance [28], even though SDC pellets or YSZ pellets coated by SDC were used as the electrolytes. Also, coating a porous LSCF cathode with a thin layer of SDC using a one-step infiltration process dramatically reduced the polarization of the LSCF cathode [29]. However, neither of the approaches studied the long term performance of the cathodes.

YSZ is chosen as the electrolyte due to its high ionic conductivity, low electronic conductivity, long-term stability and so on. Moreover, it has good compatibility with LSCF [15,30,31]. In order to decrease the effect of the electrolyte, here we use the same electrolyte for all the three cathode materials. In this work, we have developed a dip coating method to incorporate SDC into the LSCF cathode and systematically compared the electrochemical performance of the LSCF-SDC cathodes fabricated by mechanical mixing, infiltration, and dip coating with pure LSCF cathodes under the same thermal treatment conditions. To consider the effect of the interconnect, such as chromium diffusion, AISI 441 is placed on the top of the cathode. The electrochemical performance differences are evaluated. In addition, the microstructures before and after 100 h of thermal treatment are characterized. Based on these efforts, the influences of SDC on 3PBs from different LSCF-SDC cathodes during the electrochemical process are proposed.

2. Experimental procedures

2.1. Chemicals

$La(NO_3)_3 \cdot 6H_2O$, $Sr(NO_3)_2$, $Co(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Sm(NO_3)_3 \cdot 6H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$, ethylenediaminetetraacetic acid, citric acid, NH_4NO_3, sucrose and $NH_3 \cdot H_2O$ were purchased from Alfa Aesar (Ward Hill, MA). α-terpineol as solvent was purchased from Sigma–Aldrich (St. Louis, MO). Microcrystalline cellulose as a pore forming agent was purchased from Spectrum Chemical Mfg. Corp. (Gardena, CA). Ethyl cellulose as a binder was purchased from Acros Organics (New Jersey). YSZ was purchased from Nextech Materials (Lewis Center, OH). AISI 441 was produced by ATI Allegheny Ludlum Corporation (Brachenridge, PA). All other chemicals were purchased from Alfa Aesar as-received.

2.2. Synthesis of LSCF and SDC powder

Perovskite LSCF powder was synthesized by a combustion method based on the reported autocombustion method [32]. The molar ratio of $La(NO_3)_3 \cdot 6H_2O$, $Sr(NO_3)_2$, $Co(NO_3)_2 \cdot 6H_2O$, and $Fe(NO_3)_3 \cdot 9H_2O$ was 6:4:2:8 and the molar ratio of metal ions, ethylenediaminetetraacetic acid (EDTA), citric acid, ammonium nitrate, and sucrose was 2:1:2:10:0.75. In the first step, the metal nitrates were dissolved in distilled water in a beaker; EDTA, citric acid, ammonium nitrate, and sucrose were added. The pH value was adjusted by ammonium hydroxide to 6 to completely dissolve EDTA. A mesh was put over the top of the beaker, and the solution was then placed in a pre-heated furnace at 450 °C. After 10 min the combustion process was completed and the beaker was taken out to cool down. The combusted powder was then calcined at 900 °C for 2 h and milled before use. The reaction equation was as follows [33]:

$$\begin{aligned}&0.6La(NO_3)_3 + 0.4Sr(NO_3)_2 + 0.2Co(NO_3)_2 + 0.8Fe(NO_3)_3\\&\quad + C_{10}H_{16}N_2O_8 + 2C_6H_8O_7 + 10NH_4NO_3 + 0.7C_{11}H_{22}O_{11}\\&\quad + 14.15O_2 \rightarrow La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3 + 13.7N_2 + 44.25H_2O\\&\quad + 30.25CO_2\end{aligned} \tag{1}$$

SDC powder was synthesized by a sol–gel method [25]. First, stoichiometric amounts of $Sm(NO_3)_3 \cdot 6H_2O$ and $Ce(NO_3)_3 \cdot 6H_2O$ (according to the molecular composition of the oxides) were mixed into water. EDTA and citric acid were used as the chelating agents. The molar ratio of total metal ions, EDTA, and citric acid was 1:1:2. The ammonium hydroxide was used to adjust the pH value of the solution to 6. Water was evaporated from the solution while stirring at 80 °C, creating transparent gels which were kept at 200 °C for 2 h and calcined at 800 °C for 4 h. The SDC powder was milled before use. The specific surface area was about 11 m^2 g^{-1}.

2.3. Assembly of YSZ/cathode/AISI 441 tri-layers

The configuration of a half-cell is YSZ/cathode/AISI 441. Cathode was screen printed on YSZ and a Pt mesh was placed between the cathode and AISI 441. The cathode material (56.8 wt%) was mixed and ball-milled with microcrystalline cellulose (5.7 wt%), ethyl cellulose (1.1 wt%), and α-terpineol (36.4 wt%) for 1 h to make pastes for screen printing. The prepared pastes were screen printed on 8 mol% YSZ substrates, using a #330 mesh. The screen printed pastes were square-like with ~0.5 cm^2 area. The LSCF/YSZ structure was kept at 200 °C for 3 h and at 400 °C for 1 h to partially burn the binder and solvent and was then kept at 950 °C for 2 h to completely burn them out and bond with YSZ; a heating and cooling rate of 1 °C min^{-1} was used.

AISI 441 ferritic stainless steel piece was used as the interconnect material and cut into rectangular substrates (area: 10×10 mm^2). In order to remove the oxidized layer and obtain a scratch free flat surface, steel pieces were polished to optical finish and then ultrasonically cleaned with water and ethanol. The polished AISI 441 alloy piece was placed on the cathode side of the LSCF/YSZ bi-layer and the configuration of the tri-layer was shown in our previous paper [34].

2.4. SDC incorporation into LSCF cathodes by mixture, infiltration, and dip coating

For the mechanical mixing of SDC and LSCF, 10 wt% of SDC and 90 wt% of LSCF were mixed by vibratory milling for 1 h. The mixture was used as the cathode material and the procedures afterwards were the same as described in Section 2.3.

Infiltration and dip coating were carried out on the screen printed LSCF cathodes which were sintered at 950 °C prior. The weight percentage of SDC was also kept at ~10 wt%. Aqueous nitrate